VUV 5d – 4f luminescence of Gd^{3+} doped into CaF_2

V.N. Makhov[1], M. Kirm, S.Kh. Batygov[2], L.N. Dmitruk[2], G. Stryganyuk[3] and G. Zimmerer[3,4]

Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia
[1] P.N. Lebedev Physical Institute, Leninskii Prospect 53, 119991 Moscow, Russia
[2] General Physics Institute, Vavilov Str. 38, 119991 Moscow, Russia
[3] Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronensynchrotron DESY,
Notkestraße 85, 22607 Hamburg, Germany
[4] Institut für Experimentalphysik, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

Recent studies [1-4] have revealed that some Gd^{3+} containing wide band-gap fluoride crystals with scheelite and YF_3 structure emit VUV luminescence (hν ~ 10 eV), which is due to the interconfigurational $4f^65d - 4f^7$ transitions in the Gd^{3+} ion. In the present work the spectral and temporal characteristics of VUV luminescence from CaF_2 doped with Gd^{3+}(0.1%) and Ce^{3+}(0.05%) have been studied under excitation near and above the edge of interconfigurational $4f^7 - 4f^65d$ transitions in Gd^{3+} [5]. High-resolution (~1 Å) VUV emission and excitation spectra as well as decay kinetics of VUV luminescence have been measured using the SUPERLUMI set-up.

At low temperature the VUV (λ ~129.5 nm) luminescence has been detected from the $CaF_2:Gd^{3+},Ce^{3+}$ crystal under the excitation in the spectral region of $4f^7 - 4f^65d$ transitions in Gd^{3+} (Fig. 1). The VUV emission spectrum of $CaF_2:Gd^{3+},Ce^{3+}$ shows a narrow zero-phonon line at 77760 cm^{-1} followed by a broad side band centered at 77200 cm^{-1}, which is superimposed by the phonon fine structure with dominating vibronic line separated by ~370 cm^{-1} from the zero-phonon line. The decay time of the VUV luminescence is 8.5 ± 0.1 ns at 10 K. VUV luminescence is completely quenched at T ~ 150 K. The zero-phonon line and other features in the VUV emission spectrum well correlate with the structure observed at the onset of the Gd^{3+} $4f^7 - 4f^65d$ excitation spectrum. The obtained results clearly show that the VUV luminescence observed from the $CaF_2:Gd^{3+},Ce^{3+}$ crystal is due to $4f^65d - 4f^7$ radiative transitions in Gd^{3+}.

The orange (590-640 nm) luminescence, which is due to $4f^7$ $^6G_{7/2} - {}^6P_J$ transitions in Gd^{3+}, is also observed from CaF_2:Gd,Ce under the excitation to $4f^65d$ configuration of Gd^{3+}. Obviously there exists some probability for non-radiative relaxation from the lowest $4f^65d$ level of Gd^{3+} to closely spaced energy levels of Gd^{3+} $4f^7$ configuration that will finally result in the population of the emitting $4f^7$ $^6G_{7/2}$ level. The excitation spectrum of VUV luminescence completely coincides with the excitation spectrum of this orange luminescence, as expected (see Fig. 1).

Several features in the excitation spectrum can be tentatively ascribed to zero-phonon lines accompanied by the dominating vibronic lines separated by ~ 370 cm^{-1} from zero-phonon lines, similar to the Gd^{3+} $4f^65d - 4f^7$ emission spectrum. We are not aware of any theoretical calculations of $4f^7 - 4f^65d$ transitions in Gd^{3+} and hence, the detailed analysis of the structure of excitation spectrum cannot be performed. However, the energy range and many features of this structure correspond well to the energy level system of the ground ^7F_J multiplet of the $4f^6$ core in Gd^{3+} $4f^65d$ configuration as can be seen in Fig. 1, where the energy level structure of the $4f^6$ ^7F_J multiplet of Eu^{3+} (in LaF_3) is superimposed on the Gd^{3+} excitation spectrum with the ground level coinciding with the lowest-energy zero-phonon line. The decrease of VUV emission intensity towards higher energies is obviously due to the edge of intrinsic absorption of the host crystal, the energy of which can be estimated from the excitation spectrum of self-trapped exciton emission from CaF_2.

Well resolved fine structure due to zero-phonon lines and vibronic lines along with broad side-bands observed in VUV emission and excitation spectra of $CaF_2:Gd^{3+},Ce^{3+}$ indicate intermediate electron-lattice coupling between the $4f^65d$ electronic configuration of the Gd^{3+} ion and the lattice vibrations in $CaF_2:Gd^{3+},Ce^{3+}$ system. The estimation of the Huang-Rhys parameter $S \sim 1.5$ from the energy difference between the zero-phonon line and the maximum of the wide side band, taking into account the energy of the dominating vibronic line in the obtained spectra, confirms this conclusion.

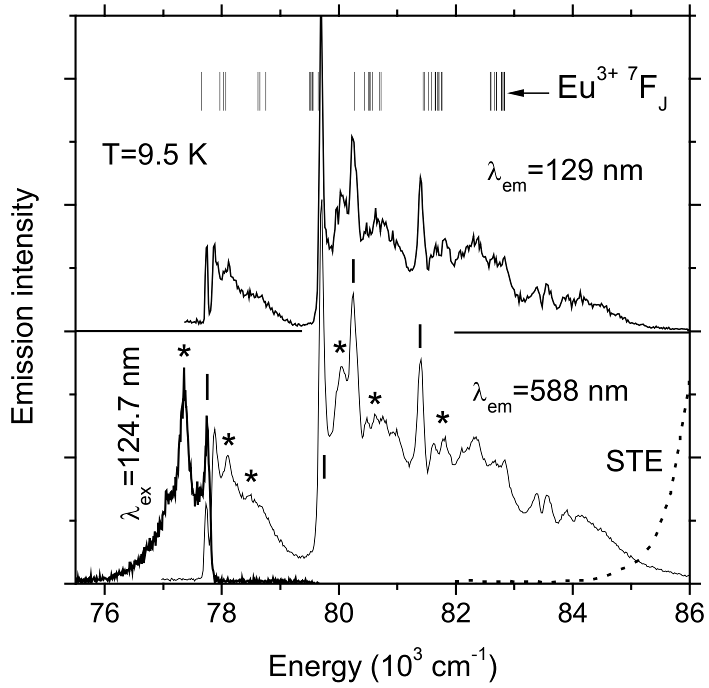

Figure 1: Spectra of $CaF_2:Gd^{3+}$(0.1%),Ce^{3+}(0.05%) crystal in the region of Gd^{3+} $4f^7 - 4f^65d$ transitions. High-resolution ($\Delta\lambda$ ~1 Å) VUV emission spectrum under 124.7 nm excitation (bold solid line). High-resolution ($\Delta\lambda$ ~ 1 Å) excitation spectra of Gd^{3+} $4f^7$ $^6G_{7/2} - {}^6P_J$ emission (lower thin solid line) and Gd^{3+} $4f^65d - 4f^7$ emission (upper thin solid line). Excitation spectrum of self-trapped exciton emission (dotted line). The spectral lines tentatively ascribed to zero-phonon lines are marked by symbol " | ", and to dominating vibronic lines by symbol " ∗ ". The energy level structure of the $4f^6$ ^7F_J ground multiplet of Eu^{3+} (in LaF_3) is superimposed on the spectra in the upper part of the Figure. T = 9.5 K.

The vibronic structure in emission and excitation spectra of Gd^{3+} $d - f$ luminescence from the $CaF_2:Gd^{3+},Ce^{3+}$ crystal differs from that observed for other trivalent rare earth ions doped into CaF_2 and is dominated by the line at ~370 cm^{-1} which does not correspond to any well-defined peak in phonon spectrum of CaF_2. This can indicate that Gd^{3+} ions reside in CaF_2 predominantly in sites of different type than other rare earth ions, and some pseudo-local mode (where the atomic amplitudes near the mass defect are changed) with the energy ~370 cm^{-1} is involved in electron-lattice coupling between the $4f^65d$ electronic configuration of the Gd^{3+} ion and the lattice vibrations in CaF_2.

This work was supported by the RFBR Grant 05-02-1730, Estonian Science Foundation (Grant 6538) and the European Community Research Infrastructure Action within the FP6 Program through the Contract RII3-CT-2004-506008 (IA-SFS).

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